The « Who am I ?» Game in Capillary Electrophoresis:

When Theory Meets Practice

Hervé Cottet[1], Hengfu Wu[2], Stuart A. Allison[2]

[1] *IBMM, University of Montpellier, CNRS, ENSCM, Montpellier, France*

[2] *Department of Chemistry, Georgia State University, Atlanta, Georgia, USA*

Imagine that you have an unknown sample containing one (or more) solute(s). You have no information on these solutes and you want to get as much information as possible on them using capillary electrophoresis instrumentation. Typically, the analytical challenge consists in finding the nature (small ion, nanoparticle, polyelectrolyte), the charge and the size of the solutes. In this work, we demonstrate that, if the knowledge of the effective electrophoretic mobility (μ_{ep}) at a single ionic strength is not sufficient to characterize a given solute, the determination of two effective electrophoretic mobilities at two different ionic strengths combined with the hydrodynamic radius (R_h), are sufficient to deduce the nature, the size and the charge of the solute [1, 2]. μ_{ep} and R_h determinations are experimentally accessible by CE and Taylor dispersion analysis, respectively, performed on the same instrumentation.

From the two μ_{ep} values, it is possible to estimate the relative decrease of the electrophoretic mobility according to the ionic strength via the introduction of a dimensionless S parameter. 3D representation of (μ_{ep}, S, R_h) data points, also called 3D slope plot, is proposed to visualize the differences in the electrophoretic behavior between solutes according to their charge and nature. Surprisingly, such 3D slope plot in the case of small ions and nanoparticles looks like a 'whale-tail', while polyelectrolyte contour plot represents a rather simple and monotonous map which is independent of solute size [2].

The decrease of the electrophoretic mobility with the ionic strength estimated by the S parameter is due to different phenomena (electrophoretic effect, internal field effect, relaxation effect and nonlinear electrostatics), the contribution of which depends both on the charge and the size of the solute in a complicated manner. This complexity in the ionic strength dependence of the electrophoretic mobility with charge and size can be better visualized on 2D (μ_{ep}, S) or 3D (μ_{ep}, S, R_h) slope plots. Reversely, the slope plot approach can be used practically to get rapid and clear information about solute charge and nature for many practical CE applications. Examples of practical use of the slope plot approach will be given for the characterization of proteins, cosmetic ingredients (aluminum chlorohydrate) or nano-sized drug delivery systems.

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[2] H. Cottet, H. Wu, S. A. Allison, Electrophoresis, 2017, 38, 624-632.